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(54) DISAZO DYES CONTAINING A FLUOROSULPHONYL GROUP AND USE THEREOF

DISAZOFARBSTOFFE ENTHALTEND EINE FLUOROSULFONYLGRUPPE UND IHRE
VERWENDUNG

COLORANTS DISAZO CONTENANT UN GROUPE FLUOROSULFONYLE ET LEUR UTILISATION

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Description

The present invention relates to a process for colouring aromatic polyester textile materials, to aromatic polyester textile materials when coloured, to a process for the mass coloration of plastics, to plastics when coloured, to certain novel azo dyes and to compositions containing azo dyes.

5 Bisazo dyes including water-solubilising groups are disclosed in FR-A-1307200 and US-A-3131021. Bisazo dyes including ice colour coupling components are disclosed in US-A-2427995. JP-A-54050021 discloses a bisazo dye in the context of reactive disperse dyes for cellulose.

10 According to the present invention there is provided a process for colouring an aromatic polyester textile material or fibre blend thereof which comprises applying to the aromatic polyester textile material a compound, which is free from water solubilizing groups, of Formula (1) :



Formula (1)

15 wherein:

A, D and E each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of A, D or E carries directly at least one $-\text{SO}_2\text{F}$ group or carries a substituent to which at least one $-\text{SO}_2\text{F}$ group is attached.

The presence of one or more $-\text{SO}_2\text{F}$ groups in a dye molecule generally improves the properties of that dye and confers surprisingly good wet-fastness and light-fastness properties.

Different compounds of Formula (1) may be mixed or the compounds of Formula (1) may be mixed with dyes which 25 do not contain an $-\text{SO}_2\text{F}$ group; such mixtures are a feature of the present invention. The mixtures may be simple physical mixtures or may be mixed crystals formed for example by co-crystallisation. Such mixtures generally show improvement in dyeing properties. Crystalline modifications of compounds of Formula (1) exist and the present definition includes such crystalline modifications which may be formed by heat treatment.

The aromatic polyester textile material is preferably polyethylene terephthalate. Fibre blends may comprise mixtures 30 of aromatic polyester with different synthetic textile materials for example secondary cellulose acetate, cellulose triacetate, polyamide, such as poly hexamethylene adipamide, and/or polyacrylonitrile or mixtures of aromatic polyester and natural textile materials. Preferred fibre blends are those of polyester-cellulose such as polyester-cotton. The textile materials or blends thereof may be in the form of filaments, loose fibres, yarn, woven or knitted fibres.

The dyes of Formula (1) preferably have low solubility in water, typically less than 1% preferably less than 0.5% 35 and especially less than 0.2% solubility in water. The dyes of Formula (1) are thus free from water solubilising groups such as $-\text{SO}_3\text{H}$, $-\text{CO}_2\text{H}$, $-\text{PO}_3\text{H}$ and quaternary amino.

The dyes of Formula (1), optionally in conjunction with other disperse dyes may be applied to the aromatic polyester 40 textile materials or fibre blends thereof by methods which are conventionally employed in dyeing disperse dyes to such materials and fibre blends. For example, the dyes of Formula (1) in the form of an aqueous dispersion may be applied by dyeing, padding or printing processes using the conditions and additives conventionally used in carrying out such processes.

The process conditions may be selected from the following:

- i) exhaust dyeing at a pH of from 4 to 6.5, at a temperature of from 125°C to 140°C for from 10 to 120 minutes and under a pressure of from 1 to 2 bar, in which a sequestrant may optionally be added;
- ii) continuous dyeing at a pH of from 4 to 6.5, at a temperature of from 190°C to 225°C for from 15 seconds to 5 minutes, in which a migration inhibitor may optionally be added;
- iii) printing direct at a pH of from 4 to 6.5, at a temperature of from 160°C to 185°C for 4 to 15 minutes for high temperature steaming, or at a temperature of from 190°C to 225°C for 15 seconds to 5 minutes for bake fixation with dry heat or at a temperature of from 120°C to 140°C and 1 to 2 bar for 10 to 45 minutes for pressure steaming, in which wetting agents and thickeners (such as alginates) of from 5 to 100% by weight of the dye may optionally be added;
- iv) discharge printing (by padding the dye onto the textile material, drying and overprinting) at a pH of from 4 to 6.5, in which migration inhibitors and thickeners may optionally be added;
- v) carrier dyeing at a pH of from 4 to 6.5, at a temperature of from 95°C to 100°C using a carrier such as methyl-naphthalene, diphenylamine or 2-phenylphenol, in which sequesterants may optionally be added; and
- vi) atmospheric dyeing of blends comprising acetate, triacetate and nylon at a pH of from 4 to 6.5, at a temperature of 85°C for acetate or at a temperature of 90°C for triacetate and nylon for from 15 to 90 minutes, in which se-

questerants may optionally be added.

In all the above processes the compound of Formula (1) is applied as a dispersion comprising from 0.001% to 4% of the compound in aqueous medium.

5 The present compounds generally provide coloured textile material which shows good fastness to washing, light and heat. The heterocyclic group represented by A, D or E may be selected from thienyl, thiazolyl, isothiazolyl, pyrazolyl, imidazolyl, pyridyl, pyridonyl, 1,2,4- and 1,3,4-thiadiazolyl, furanyl, pyrrolyl, pyridazyl, pyrimidyl, pyrazinyl, benzothiazolyl, benzoisothiazolyl, quinolinyl, isoquinolinyl, indolyl, pyridothiazolyl, pyridoisothiazolyl, 1,2,3- and 1,2,4-triazolyl. The carbocyclic group represented by A, D or E may be phenyl or naphthyl.

10 A and E each independently is preferably thienyl, phenyl, naphthyl, thiazolyl, isothiazolyl, pyridonyl, more preferably thien-2-yl, phenyl, naphthyl, thiazol-2-yl, isothiazol-5-yl or pyrid-4-one-5-yl and especially phenyl or naphthyl.

D is preferably phenyl, naphthyl, biphenyl, thienyl or thiazolyl, more preferably phen-1,4-ylene, naphth-1,4-ylene, 4,4'-biphenylene, 3,3'-dichloro-4,4'-biphenylene, thien-2,5-ylene or thiazol-2,5-ylene and especially phen-1,4-ylene, naphth-1,4-ylene or thien-2,5-ylene.

15 Examples of suitable substituents for A, D and E are cyano, nitro, halo such as fluoro, chloro and bromo, fluorosulphonyl, trifluoromethyl, alkyl, alkoxy, aryloxy, -COalkyl, -NHOalkyl, -NHSO₂alkyl, -OCOalkyl, -Salkyl, -Saryl, -SO₂alkyl, -SO₂aryl, NR¹R², -CONR¹R², -SO₂NR¹R² in which R¹ and R² each independently is -H or cycloalkyl, alkyl, alkyl or alkoxy substituted by -OH, -CN, halo such as -F, -Cl and -Br, phenyl, -SO₂F, -OCOalkyl, -COOalkyl,

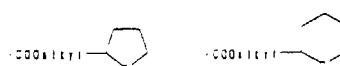
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25 -OCOPhenyl, -COOPhenyl, -OCO(fluorosulphonylphenyl), alkyl(fluorosulphonylphenyl), -OCO (fluorosulphonylphenyl), -COOalkoxyalkoxy, alkoxyalkoxy, -OCalkyl, -OCalkoxyalkoxy, alkenyl, -OCOalkenyl, -COOalkylOalkyl, -OalkylCN, alkoxy, aryloxy, -OalkylOCOalkylOalkyl in which each alkyl is C₁₋₁₀-alkyl and each alkoxy is C₁₋₁₀-alkoxy each of which may be straight or branched chain and each alkyl, alkoxy, aryl or phenyl group may carry an -SO₂F substituent or R¹ and R² together with the -N atom to which they are attached form a 5- or 6-membered ring such as morpholino or piperidino.

30 Preferred substituents for A, D and E are cyano, nitro, chloro, bromo, fluorosulphonyl, C₁₋₆-alkyl, C₁₋₆-alkoxy, -COC₁₋₆-alkyl, -NHCO₁₋₆-alkyl, -OCOC₁₋₆-alkyl, -COOC₁₋₆-alkyl, -NR¹R² in which R¹ and R² each independently is -H, C₁₋₆-alkyl, C₁₋₆-alkyl substituted by -OH, -CN, -Cl, phenyl, -OCOC₁₋₆-alkyl, -COOC₁₋₆-alkyl,

35



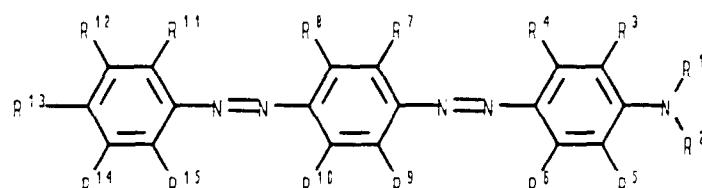
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C₁₋₄-alkyl(4-fluorosulphonylphenyl), OCO(3-fluorosulphonylphenyl), -OCOPhenyl, -OCO(4-fluorosulphonyl), -C₂₋₄-alkenyl, -COOC₁₋₆-alkylOOC₁₋₆-alkyl, -OC₁₋₆-alkylCN, -OC₁₋₆-alkylOCOC₁₋₆-alkyl or where R¹ and R² together with the -N atom to which they are attached form a morpholino or piperidino.

45 The compounds of Formula (1) preferably carry a total of from one to three -SO₂F groups, more preferably from one to two -SO₂F groups and especially one -SO₂F group.

A preferred sub-group of compounds of Formula (1) are those of Formula (2):

50



55

Formula (2)

in which:

R¹ and R²

each independently is -H, C₁₋₈-alkyl or C₁₋₆-alkyl substituted by -OH, -CN, -F, -Cl, -Br, -SO₂F, phenyl, phenylSO₂F, -OCOC₁₋₆-alkyl, -COOC₁₋₆-alkyl, -COOC₁₋₆-alkoxyC₁₋₆-alkoxy, C₁₋₆-alkoxy, C₁₋₆-alkoxyC₁₋₆-alkoxy, -OCC₁₋₆-alkyl, -OCC₁₋₆-alkoxyC₁₋₆-alkoxy, -OC(3-fluorosulphonylphenyl), -OC(4-fluorosulphonylphenyl), -OCOPhenyl, or -OCOC₂₋₄-alkenyl;

R³

is -H, -SO₂F, C₁₋₆-alkyl or C₁₋₆-alkoxy;

R⁴

is -H, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy or -NHCOC₁₋₆-alkyl;

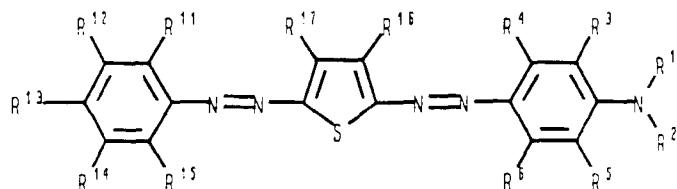
R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰

each independently is -H, C₁₋₆-alkyl, C₁₋₆-alkoxy or -SO₂F;

R¹¹, R¹², R¹³, R¹⁴ and R¹⁵

each independently is -H, -CN, -NO₂, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy, -COOC₁₋₆-alkyl, -COOC₁₋₆-alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² in which R¹ and R² are as hereinbefore defined.

In compounds of Formula (2) R⁷, R⁸, R⁹ and R¹⁰ each independently is preferably -H, C₁₋₆-alkyl or C₁₋₆-alkoxy.
A further preferred sub-group of compounds of Formula (1) are those of Formula (3):



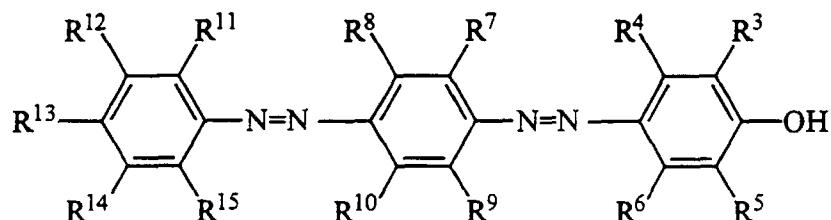
Formula (3)

in which:

R¹, R², R³, R⁴, R⁵, R⁶, R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ are as hereinbefore defined for compounds of Formula (2); and
R¹⁶ is -H, -CN, -SO₂F, -COOC₁₋₆-alkyl, -COOC₁₋₆-alkyl or -CONR¹R² in which R¹ and R² are as hereinbefore defined; and
R¹⁷ is -H, -CN, -SO₂F or C₁₋₆-alkyl.

In compounds of Formula (3) R¹⁶ is preferably -H, -CN, -COOC₁₋₆-alkyl, -COOC₁₋₆-alkyl or -CONR¹R² and R¹⁷ is preferably -H, -CN or C₁₋₆-alkyl.

A further preferred subgroup of compounds of Formula (1) are those of Formula (4):



Formula (4)

in which R³ to R¹⁵ are as hereinbefore defined.

In a further preferred embodiment of the present invention the compounds of Formulae (1), (2), (3) and (4) carry directly at least one -SO₂F group or carry a substituent to which at least one -SO₂F group is attached and carry at least one ester group or carry a substituent to which at least one ester group is attached. Such dyes with both -SO₂F and

ester groups show improved dyeing properties, particularly wet-fastness and light-fastness.

Compositions comprising dispersions of the compounds of Formulae (1), (2), (3) or (4) in which A, D and E are as hereinbefore defined in aqueous media are novel and from a further feature of the present invention. The compositions typically comprise from 1% to 30% of a compound of Formulae (1), (2) or (3) and are preferably buffered at a pH from 2 to 7, more preferably at a pH from 4 to 6.

These dispersions may further comprise ingredients conventionally used in dyeing applications such as dispersing agents for example lignosulphonates, naphthalene sulphonic acid/formaldehyde condensates or phenol/cresol/sulph-anilic acid/formaldehyde condensates, surfactants, wetting agents such as alkyl aryl ethoxylates which may be sulphonated or phosphated, inorganic salts de-foamers such as mineral oil or nonanol, organic liquids and buffers. Dispersing agents may be present at from 10% to 200% on the weight of the compound of Formula (1). Wetting agents may be used at from 0% to 20% on the weight of the compound of Formula (1). The dispersions may be prepared by bead milling the compound of Formula (1) with glass beads or sand in an aqueous medium.

According to a further feature of the present invention there is provided a process for the mass coloration of plastics which comprises incorporating into a plastics material a compound or mixture thereof which is free from water solubilising groups, of Formula (1) in which A, D and E each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of A, D or E carries directly at least one $-SO_2F$ group or carries a substituent to which at least one $-SO_2F$ group is attached.

The plastics may be selected from polystyrene, acrylics, styrene/acrylonitrile mixtures, acrylonitrile/butadiene/styrene mixtures, polycarbonate, polyether-sulphone, nylons, rigid PVC (uPVC) and polypropylene.

The compound may be incorporated by blending with granules or powdered plastics material by, for example, dry tumbling or highspeed mixing followed by injection moulding on a screw machine or by conventional compounding/masterbatching techniques. The present dyes generally dissolve or disperse readily in hot plastics melt and provide bright coloration generally with good clarity and good light fastness.

The plastics materials when coloured with the above dyes form a further feature of the present invention.

The compounds of Formula (1) may be prepared by usual methods for the preparation of disazo compounds such as by diazotisation of an amine $A-NH_2$ and coupling onto a component $X-D-NH_2$ in which A and D are as hereinbefore defined and X is a group displaceable by a diazotised amine, followed by diazotisation of the resultant monoazo compound $A-N=N-D-NH_2$ and coupling onto a component E-X in which E and X are as hereinbefore defined.

Typically the amine $A-NH_2$ may be diazotised in an acidic medium such as acetic or propionic acid or mixtures thereof using a nitrosating agent such as nitrosyl sulphuric acid at a temperature from -5°C to 5°C. The diazotised amine may be coupled onto the component $X-D-NH_2$ in an alkanol such as methanol and water at a temperature of from 0°C to 5°C. The monoazo compound $A-N=N-D-NH_2$ may be recovered from the reaction mixture by filtration. The $A-N=N-D-NH_2$ may be diazotised in an acidic medium such as acetic or sulphuric acid or mixtures thereof using a nitrosating agent as described above and coupled onto a component E-X in aqueous medium preferably whilst maintaining the pH at about 3. The $A-N=N-D-N=N-E$ product may be recovered from the reaction mixture by filtration and may be purified by slurring in an alkanol such as methanol and refiltering.

Fluorosulphonyl groups may be introduced into the compounds of Formula (1) or into the A, D and E components prior to coupling by methods generally available in the literature. For example reaction of the compound of Formula (1), $A-NH_2$, the NH_2 being protected as necessary, D-X in which A and D are as hereinbefore defined, with chlorosulphonic acid optionally in the presence of dimethylformamide and thionylchloride at a temperature of from 30°C to 100°C gives the chlorosulphonyl derivative. The chlorosulphonyl derivative may be reacted in boiling aqueous media with potassium fluoride to give the fluorosulphonyl derivative.

Alternatively the compound of Formula (1), $A-NH_2$, or D-X may be sulphonated with sulphuric acid or oleum to give the sulphonic acid derivative which may be converted to the chlorosulphonyl derivative by reaction, either of the free acid or an inorganic salt thereof, with thionylchloride optionally in the presence of a chlorophosphorus compound such as phosphorus oxychloride or phosphorus pentachloride in an organic liquid such as an aromatic hydrocarbon at a temperature of from 20°C to 110°C. The chlorosulphonyl derivative may then be converted to the fluorosulphonyl derivative as described above.

The compound of Formula (1) is useful for the coloration of synthetic textile materials particularly polyester textile materials and fibre blends thereof to which they impart colours which are excellent wet and light fastness properties.

The invention is further illustrated by the following Examples.

Example 1

4-Aminobenzenesulphonyl fluoride (4 parts) was stirred in acetic/propionic acid 86/14 vol/vol (250 parts) at 0-5°C. While maintaining the temperature below 10°C, 40% nitrosyl sulphuric acid (4.8 parts) was added carefully and stirred for 1.5 hours before adding slowly to 2-amino-3-cyanothiophene (4.2 parts) in methanol (625 parts) and ice/water (840 parts). The pH was maintained at 3 by the addition of sodium acetate and 50% sodium hydroxide solution. After stirring

at 0-5°C for a further 2 hours filtration yielded 3.3 parts of 2-amino-3-cyano-5-(4'-sulphonylfluorophenylazo)thiophene.

2-Amino-3-cyano-5-(4'-sulphonylfluorophenylazo)thiophene (12.5 parts) was stirred in glacial acetic acid (830 parts) at 15°C while 50% sulphuric acid (375 parts) was added slowly. On cooling further to 0-5°C, 40% nitrosyl sulphuric acid (18 parts) was added carefully and the reaction stirred for 2 hours before adding slowly, while maintaining the pH at 3 by the addition of 50% sodium hydroxide solution, to a mixture of N,N-bis- (p-acetoxyethyl)-aniline (15 parts) in ice/water (960 parts), sulphamic acid (10 parts) and saturated sodium acetate solution (50 parts). The product was isolated by filtration, washed with water and pulled dry. The damp solid was then slurried in methanol (100 parts), refiltered and dried overnight to yield 4-(3-cyano-5-(4'-sulphonylfluorophenylazo)-2-thiophene-azo)-N,N-bis-(p-acetoxyethyl)-aniline (4 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades.

10

Example 2

The procedure for Example 1 was repeated except that in place of 15 parts of N,N-bis-(p-acetoxyethyl)-aniline; 15 parts of N- (2-cyanoethyl) -N- (2-methoxy-carbonylethyl)-m-toluidine were used to yield 4- (3-cyano-5- (4'-sulphonylfluorophenylazo)-2-thiophene-azo)-N-(2-cyanoethyl)-N- (2-methoxy-carbonylethyl)-m-toluidine (3.8 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades.

Example 3

The procedure for Example 1 was repeated except that in place of 15 parts of N,N-bis- (p-acetoxyethyl)-aniline; 15 parts N,N-bis-(2-cyanoethyl)-aniline were used to yield the product 4-(3-cyano-5-(4'-sulphonylfluoro-phenyl azo)-2-thiophene-azo)-N,N-bis-(2-cyanoethyl)-aniline (2.2 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades. λ_{\max} 575nm.

Example 4

The procedure for Example 1 was repeated except that in place of 15 parts of N,N-bis-(p-acetoxyethyl)-aniline; 15 parts of N-ethyl-N- (2-carboxyethyl) -aniline were used to yield the product 4-(3-cyano-5-(4'-sulphonylfluorophenylazo)-2-thiophene-azo)-N-ethyl-N-(2-carboxyethyl) -aniline (2.4 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades. λ_{\max} 637nm.

Example 5

The procedure for Example 1 was repeated except that in place of 15 parts of N,N-bis- (p-acetoxyethyl)-aniline; 15 parts of N,N-diethyl m-acetanilide were used to yield the product 4-(3-cyano-5-(4'-sulphonylfluorophenylazo)-2-thiophene-azo)-N,N-diethyl m-acetanilide (6.5 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades.

Example 6

3-Aminobenzenesulphonyl fluoride hydrochloride hydrate (4 parts) was stirred in acetic/propionic acid 86/14 vol/vol (250 parts) at 0-5°C. While maintaining the temperature below 10°C, 40% nitrosyl sulphuric acid (4.8 parts) was added carefully and stirred for 1.5 hours before adding slowly to 2-amino-3-cyanothiophene (4.2 parts) in methanol (625 parts), ice/water (840 parts). The pH was maintained at 3 by the addition of sodium acetate and 50% sodium hydroxide solution. After stirring at 0-5°C for a further 2 hours filtration yielded 3.3 parts of 2-amino-3-cyano-5-(3'-sulphonyl fluoro-phenylazo)-thiophene.

2-Amino-3-cyano-5-(3'-sulphonylfluoro-phenylazo)-thiophene (12.5 parts) was stirred in glacial acetic acid (830 parts) at 15°C while 50% sulphuric acid (375 parts) was added slowly. On cooling further to 0-5°C, 40% nitrosyl sulphuric acid (18 parts) was added carefully and the reaction stirred for 2 hours before adding slowly, while maintaining the pH at 3 by the addition of 50% sodium hydroxide solution, to a mixture of N,N-diethylaniline (15 parts) was stirred in ice/water (960 parts), sulphamic acid (10 parts) and saturated sodium acetate solution (50 parts). The diazo (12.5 parts) was then added slowly. The product was isolated by filtration, washed with water and pulled dry. The damp solid was then slurried in methanol (100 parts), refiltered then washed with water to yield 4-(3-cyano-5-(3'-sulphonylfluorophenylazo)-2-thiophene-azo)-N,N-diethyl aniline (1.7 parts). When applied to polyester materials from an aqueous dispersion, the dye gave blue shades.

Example 7

The procedure for Example 6 was repeated except that in place of 15 parts of N,N-diethyl aniline; 15 parts of N-ethyl-N-(2-cyanoethyl) aniline were used to yield the product 4-(3-cyano-5-(3'-sulphonylfluorophenylazo)-2-thiophene-azo)-N-ethyl-N-(2-cyanoethyl) aniline (7 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades.

Example 8

10 The procedure for Example 6 was repeated except that in place of 15 parts of N,N-diethyl aniline; 15 parts of N-(2-cyanoethyl)-N-(acetoxymethyl)aniline were used to yield the product 4-(3-cyano-5-(3'-sulphonylfluorophenylazo)-2-thiophene-azo)-N-(2-cyanoethyl)-N-(acetoxymethyl) aniline (2 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades. λ_{max} 585nm.

Example 9

15 The procedure for Example 6 was repeated except that in place of 15 parts of N,N-diethyl aniline; 15 parts of N-octyl-N-(sec)butyl-aniline were used to yield the product 4-(3-cyano-5-(3'-sulphonylfluorophenylazo)-2-thiophene-azo)-N-octyl-N-(sec)butyl-aniline (1.5 parts) which when applied to polyester materials from an aqueous dispersion gave blue/green shades.

Example 10

20 The procedure for Example 6 was repeated except that in place of 15 parts of N,N-diethyl aniline; 15 parts of N-
25 N-diethyl m-acetanilide were used to yield the product 4-(3-cyano-5-(3'-sulphonylfluorophenylazo)-2-thiophene-azo)-N,N-diethyl m-acetanilide (3 parts) which when applied to polyester materials from an aqueous dispersion gave blue/
green shades.

Example 11

30 The procedure for Example 6 was repeated except that in place of 15 parts of N,N-diethyl aniline; 15 parts of N-
35 butyl-N-secbutyl m-acetanilide were used to yield the product 4-(3-cyano-5-(3'-sulphonylfluorophenylazo)-2-thiophene-azo)-N-butyl-N-sec-butyl m-acetanilide (8.5 parts) which when applied to polyester materials from an aqueous dispersion gave blue/green shades.

Example 12

40 The procedure for Example 6 was repeated except that in place of 15 parts of N,N-diethyl aniline; 15 parts of N-
45 ethyl-N-benzylaniline were used to yield the product 4-(3-cyano-5-(3'-sulphonylfluorophenylazo)-2-thiophene-azo)-N-
ethyl-N-benzyl-aniline (2.3 parts) which when applied to polyester materials from an aqueous dispersion gave blue
shades.

Example 13

50 The procedure for Example 6 was repeated except that in place of 15 parts of N,N-diethylaniline; 15 parts of N-
55 ethyl-N-2-isopropenoxy carbonyl ethylaniline were used to yield the product 4-(3-cyano-5-(3'-sulphonylfluorophenylazo)-2-thiophene-azo)-N-ethyl-N-2-isopropenoxy carbonyl-ethyl-aniline (2 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades.

Example 14

3-Amino-4-methoxybenzenesulphonyl fluoride (4 parts) was stirred in acetic/propionic acid 86/14 vol/vol (250 parts) at 0-5°C. While maintaining the temperature below 10°C, 40% nitrosyl sulphuric acid (4.8 parts) was added carefully and stirred for 1.5 hours before adding slowly to 2-amino-3-cyanothiophene (4.2 parts) in methanol (625 parts), ice/water (840 parts). The pH was maintained at 3 by the addition of sodium acetate and 50% sodium hydroxide solution. After stirring at 0-5°C for a further 2 hours filtration yielded 3.2 parts of 2-amino-3-cyano-5-(2'-methoxy-5'-sulphonylfluorophenylazo)-thiophene.

2-Amino-3-cyano-5-(2'-methoxy-5'-sulphonylfluorophenylazo)-thiophene (12.5 parts) was stirred in glacial acetic

acid (830 parts) at 15°C while 50% sulphuric acid (375 parts) was added slowly. On cooling further to 0-5°C, 40% nitrosyl sulphuric acid (18 parts) was added carefully and the reaction stirred for 2 hours before adding slowly, while maintaining the pH at 3 by the addition of 50% sodium hydroxide solution, to a mixture of N-(2-cyanoethyl)-N-acetoxyethylaniline (15 parts) was stirred in ice/water (960 parts), sulphamic acid (10 parts) and saturated sodium acetate solution (50 parts). The product was isolated by filtration, washed with water and pulled dry. The damp solid was then slurried in methanol (100 parts), refiltered then washed with water to yield 4-(3-cyano-5-(2'-methoxy-5'-sulphonylfluorophenylazo)-2-thiophene-azo)-N,N-diethyl aniline (3 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades.

10 Example 15

The procedure for Example 14 was repeated except that in place of 15 parts of N-(2-cyanoethyl)-N-acetoxyethylaniline; 15 parts of N-butyl-N-(2-cyanoethyl) aniline were used to yield the product 4-(3-cyano-5-(2'-methoxy-5'-sulphonylfluorophenylazo)-2-thiophene-azo)-N-butyl-N-(2-cyanoethyl)aniline (6 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades.

Example 16

3-Aminobenzenesulphonylfluoride hydrochloride hydrate (4 parts) was stirred in acetic/propionic acid 86/14 vol/vol (250 parts) at 0-5°C. While maintaining the temperature below 10°C, 40% nitrosyl sulphuric acid (4.8 parts) was added carefully and stirred for 1.5 hours before adding slowly to 2-amino-3-ethoxycarbonyl-thiophene (4.2 parts) in methanol (625 parts), ice/water (840 parts). The pH was maintained at 3 by the addition of sodium acetate and 50% sodium hydroxide solution. After stirring at 0-5°C for a further 2 hours filtration yielded 3.3 parts of 2-amino-3-ethoxycarbonyl-5-(3'-sulphonylfluorophenylazo)thiophene.

25 2-Amino-3-ethoxycarbonyl-5-(3'-sulphonylfluorophenylazo)-thiophene (12.5 parts) was stirred in glacial acetic acid (830 parts) at 15°C while 50% sulphuric acid (375 parts) was added slowly. On cooling further to 0-5°C, 40% nitrosyl sulphuric acid (18 parts) was added carefully and the reaction stirred for 2 hours before adding slowly, while maintaining the pH at 3 by the addition of 50% sodium hydroxide solution, to N-ethyl-N-(2-cyanoethyl)-aniline (15 parts) was stirred in ice/water (960 parts), sulphamic acid (10 parts) and saturated sodium acetate solution (50 parts). The product was isolated by filtration, washed with water and pulled dry. The damp solid was then slurried in methanol (100 parts), refiltered then washed with water to yield 4-(3-ethoxycarbonyl-5-(3'-sulphonylfluoro-phenyl-azo)-2-thiophene-azo)-N-ethyl-N-(2-cyanoethyl)-aniline (2.7 parts) which when applied to polyester materials from an aqueous dispersion gave blue shades.

35 Example 17

The procedure for Example 1 was repeated except that in place of 15 parts of N,N-bis- (p-acetoxyethyl)-aniline; 15 parts of N-ethyl-N-(4-sulphonylfluorophenyl)-propyl)-aniline was used to yield the product 4-(3-cyano-5-(4'-sulphonylfluoro-phenylazo)-2-thiophene-azo)-N-ethyl-N-((4-sulphonylfluorophenyl)-propyl)-aniline (0.25 parts). When applied to polyester materials from an aqueous dispersion, the dye gave blue shades, λ_{\max} 649nm.

Example 18

The procedure for Example 6 was repeated except that in place of 15 parts of N,N-diethylaniline; 15 parts of N-ethyl-N-((4-sulphonylfluorophenyl)-ethyl)-aniline was used to yield the product 4-(3-cyano-5-(3'-sulphonylfluoro-phenylazo)-2-thiophene-azo)-N-ethyl-N-((4-sulphonylfluorophenyl)-ethyl)-aniline (4 parts). When applied to polyester materials from an aqueous dispersion, the dye gave blue shades, λ_{\max} 629 nm.

Example 19

The procedure for Example 14 was repeated except that in place of 15 parts of N-(2-cyanoethyl)-N-acetoxyethylaniline; 15 parts of N-ethyl-N-((4-sulphonylfluorophenyl)-ethyl)-aniline was used to yield the product 4-(3-cyano-5-(2'-methoxy-5'-sulphonylfluoro-phenyl azo)-2-thiophene-azo)-N-ethyl-N-((4-sulphonylfluorophenyl)-ethyl)-aniline (1.6 parts). When applied to polyester materials from an aqueous dispersion, the dye gave blue shades, λ_{\max} 627nm.

55 Example 20

The procedure for Example 16 was repeated except that in place of 4 parts of 3-aminobenzenesulphonyl fluoride

hydrochloride hydrate; 4 parts of 4-nitroaniline was used and in place of 15 parts of N-ethyl-N-(2-cyanoethyl)-aniline; 15 parts of N-ethyl-N-((4-sulphonylfluorophenyl)-ethyl)-aniline was used. This yielded 4-(3-ethoxycarbonyl-5-(4'-nitrophenyl-azo)-2-thiophene-azo)-N-ethyl-N-((4-sulphonylfluorophenyl)-ethyl)-aniline (1.9 parts), which when applied to polyester materials from an aqueous dispersion gave blue colours.

5 Example 21

Sulphanilyl fluoride (4 parts) was stirred in acetic/propionic acid 86/14 vol/vol (250 parts) at 0-5°C. While maintaining the temperature below 10°C, 40% nitrosyl sulphuric acid (4.8 parts) was added carefully and stirred for 1.5 hours.

10 The diazo component was then added slowly to 2,5-dimethoxyaniline (4.1 parts) in methanol (625 parts) and ice/water (840 parts). The pH was maintained at 5-6 by the addition of sodium acetate. After stirring at 0-5°C for 2 hours the mixture was allowed to warm to room temperature before being filtered to yield 3.8 parts of 2,5-dimethoxy-4-(4'-sulphonylfluorophenyl-azo)-aniline.

15 2,5-Dimethoxy-4-(4'-sulphonylfluorophenyl-azo)-aniline (8 parts) was stirred in conc. sulphuric acid (750 parts). On cooling to 0-5°C, 40% nitrosyl sulphuric acid (12 parts) was added carefully and the reaction stirred for 1 hour before being allowed to warm to room temperature.

20 N-Ethyl-N-(4'-fluorosulphonylbenzyl)-aniline (14 parts) was stirred in ice/water (960 parts), sulphamic acid (10 parts) and methanol (1250 parts). The diazo (8 parts) was then added slowly while maintaining the pH at 5-6 by the addition of sodium acetate and sodium carbonate solution. The oil obtained was taken up in dichloromethane and purified by column chromatography. Yielded 0.1 parts of the product 4-(2',5'-Dimethoxy-4-(4"-sulphonylfluorophenyl-azo)-phenylazo)-N-ethyl-N-(4'-fluorosulphonylbenzyl)-aniline, λ_{max} 536 nm.

Example 22

25 The procedure for Example 21 was repeated except that in place of 14 parts of N-ethyl-N-(4'-fluorosulphonylbenzyl)-aniline; 14 parts of N,N-dibutyl-m-toluidine was used to yield the product 4-(2',5'-Dimethoxy-4-(4"-sulphonylfluorophenyl-azo)-phenylazo)-N,N-dibutyl-toluidine (0.27 parts).

Example 23

30 The procedure for Example 23 was repeated except that the starting dye was 1-methyl-3-(4-phenylazo-phenylazo)-1H-quinolin-2-one (2.2 parts) and heating with chlorosulphonic acid was carried out for 2 hours. The product (0.6 parts) was found to be a mixture of 1-methyl-3-(4'-(4"-fluorosulphonyl-phenylazo)-phenylazo)-4-(1H-quinolin-2-onyl)-sulphonyl fluoride and 1-methyl-3-(4-phenylazo-phenylazo)-4-(1H-quinolin-2-onyl)-sulphonyl fluoride.

35

Claims

40 1. A process for colouring an aromatic polyester textile material or fibre blend thereof which comprises applying to the aromatic polyester textile material a compound which is free from water solubilising groups of Formula (1):



Formula (1)

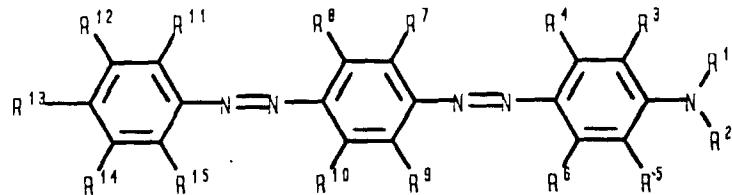
45 wherein:

A, D and E each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of A, D or E carries directly at least one $-\text{SO}_2\text{F}$ group or carries a substituent to which at least one $-\text{SO}_2\text{F}$ group is attached.

50

2. A process according to Claim 1 in which the compound of Formula (1) is of Formula (2):

55



Formula (2)

in which:

15 R¹ and R²

each independently is -H, C₁₋₆-alkyl or C₁₋₆-alkyl substituted by -OH, -CN, -F, -Cl, -Br, -SO₂F, phenyl, phenylSO₂F, -OCOC₁₋₆-alkyl, -COOC₁₋₆-alkoxyC₁₋₆-alkoxy, -COOC₁₋₆-alkoxyC₁₋₆-alkoxy, C₁₋₆-alkoxy, C₁₋₆-alkoxyC₁₋₆-alkoxy, -OCC₁₋₆-alkyl, -OCC₁₋₆-alkoxyC₁₋₆-alkoxy, -OCO(3-fluorosulphonylphenyl), -OCO(4-fluorosulphonylphenyl), -OCOPhenyl or -OCOC₂₋₄-alkenyl;

20 R³

is -H, -SO₂F, C₁₋₆-alkyl or C₁₋₆-alkoxy;

R⁴

is -H, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy or -NHCOC₁₋₆-alkyl;

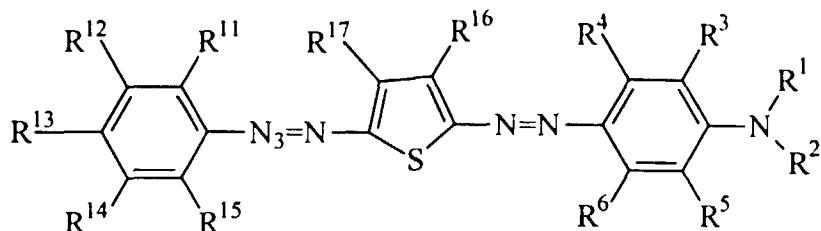
25 R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰

each independently is -H, C₁₋₆-alkyl, C₁₋₆-alkoxy or -SO₂F; and

R¹¹, R¹², R¹³, R¹⁴ and R¹⁵

each independently is -H, -CN, -NO₂, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy, -COC₁₋₆-alkyl, -COOC₁₋₆-alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² in which R¹ and R² are as hereinbefore defined.

3. A process according to Claim 1 in which the compound of Formula (1) is of Formula (3):



Formula (3)

40 in which:

45 R¹ and R²

each independently is -H, C₁₋₆-alkyl or C₁₋₆-alkyl substituted by -OH, -CN, -F, -Cl, -Br, -SO₂F, phenyl, phenylSO₂F, -OCOC₁₋₆-alkyl, -COOC₁₋₆-alkoxyC₁₋₆-alkoxy, -COOC₁₋₆-alkoxyC₁₋₆-alkoxy, C₁₋₆-alkoxy, C₁₋₆-alkoxyC₁₋₆-alkoxy, -OCC₁₋₆-alkyl, -OCC₁₋₆-alkoxyC₁₋₆-alkoxy, -OCO(3-fluorosulphonylphenyl), -OCO(4-fluorosulphonylphenyl), -OCOPhenyl or -OCOC₂₋₄-alkenyl;

50 R³

is -H, -SO₂F, C₁₋₆-alkyl or C₁₋₆-alkoxy;

R⁴

is -H, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy or -NHCOC₁₋₆-alkyl;

55 R⁵ and R⁶

each independently is -H, C₁₋₆-alkyl, C₁₋₆-alkoxy or -SO₂F;

R¹¹, R¹², R¹³, R¹⁴ and R¹⁵

each independently is -H, -CN, -NO₂, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy, -COC₁₋₆-alkyl, -COOC₁₋₆-alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² in which R¹ and R² are as hereinbefore defined;

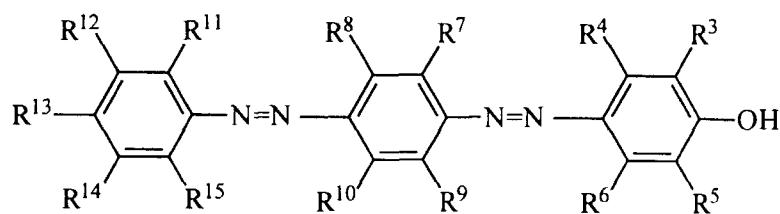
R¹⁶

is -H, -CN, -SO₂F, -COOC₁₋₆-alkyl, -COC₁₋₆-alkyl or -CONR¹R² in which R¹ and R² are as hereinbefore defined; and

R¹⁷

is -H, -CN, -SO₂F or C₁₋₆-alkyl.

4. A process according to Claim 1 in which the compound of Formula (1) is of Formula (4):

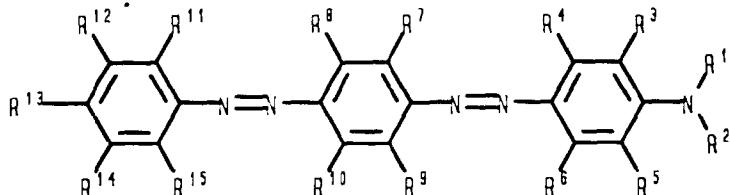


Formula (4)

15 in which:

R³ is -H, -SO₂F, C₁₋₆-alkyl or C₁₋₆-alkoxy;
R⁴ is -H, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy or -NHCOC₁₋₆-alkyl;
20 R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ each independently is -H, C₁₋₆-alkyl, C₁₋₆-alkoxy or -SO₂F; and
R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ each independently is -H, -CN, -NO₂, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy, -COC₁₋₆-alkyl, -COOC₁₋₆-alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² in which R¹ and R² are as hereinbefore defined.

- 25 5. A compound of Formula (1) as defined in Claim 1 in which the compound of Formula (1) is of Formula (2):-

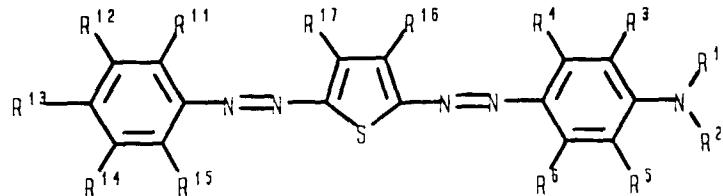


Formula (2)

35 in which:

R¹ and R² each independently is -H, C₁₋₆-alkyl or C₁₋₆-alkyl substituted by -OH, -CN, -F, -Cl, -Br, -SO₂F, phenyl, phenylSO₂F, -OCOC₁₋₆-alkyl, -COOC₁₋₆-alkoxyC₁₋₆-alkoxy, -COOC₁₋₆-alkoxyC₁₋₆-alkoxy, C₁₋₆-alkoxy, C₁₋₆-alkoxyC₁₋₆-alkoxy, -OCC₁₋₆-alkyl, -OCC₁₋₆-alkoxyC₁₋₆-alkoxy, -OCO(3-fluorosulphonylphenyl), -OCO(4-fluorosulphonylphenyl), -OCOPhenyl or -OCOC₂₋₄-alkenyl;
45 R³ is -H, -SO₂F, C₁₋₆-alkyl or C₁₋₆-alkoxy;
R⁴ is -H, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy or -NHCOC₁₋₆-alkyl;
R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ each independently is -H, C₁₋₆-alkyl, C₁₋₆-alkoxy or -SO₂F; and
R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ each independently is -H, -CN, -NO₂, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy, -COC₁₋₆-alkyl, -COOC₁₋₆-alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² in which R¹ and R² are as hereinbefore defined.

- 50 6. A compound of Formula (1) as defined in Claim 1 in which the compound of Formula (1) is of Formula (3):

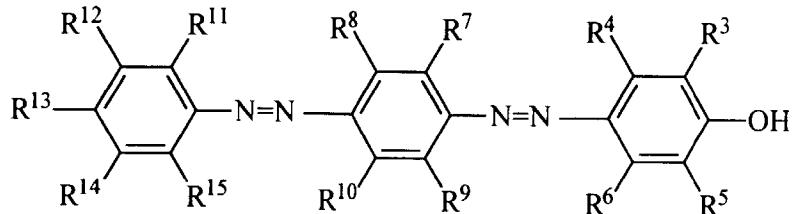


Formula (3)

in which:

- 15 R¹ and R² each independently is -H, C₁₋₆-alkyl or C₁₋₆-alkyl substituted by -OH, -CN, -F, -Cl, -Br, -SO₂F, phenyl, phenylSO₂F, -OCOC₁₋₆-alkyl, -COOC₁₋₆-alkoxyC₁₋₆-alkoxy, -COOC₁₋₆-alkoxyC₁₋₆-alkoxy, C₁₋₆-alkoxy, C₁₋₆-alkoxyC₁₋₆-alkoxy, -OCC₁₋₆-alkyl, -OCC₁₋₆-alkoxyC₁₋₆-alkoxy, -OC(3-fluorosulphonylphenyl), -OC(4-fluorosulphonylphenyl), -OCOPhenyl or -OCOC₂₋₄-alkenyl;
- 20 R³ is -H, -SO₂F, C₁₋₆-alkyl or C₁₋₆-alkoxy;
- R⁴ is -H, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy or -NHCOC₁₋₆-alkyl;
- R⁵ and R⁶ each independently is -H, C₁₋₆-alkyl, C₁₋₆-alkoxy or -SO₂F;
- R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ each independently is -H, -CN, -NO₂, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy, -COC₁₋₆-alkyl, -COOC₁₋₆-alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² in which R¹ and R² are as hereinbefore defined;
- 25 R¹⁶ is -H, -CN, -SO₂F, -COOC₁₋₆-alkyl, -COC₁₋₆-alkyl or -CONR¹R² in which R¹ and R² are as hereinbefore defined; and
- R¹⁷ is -H, -CN, -SO₂F or C₁₋₆-alkyl.

- 30 7. A compound of Formula (1) as defined in Claim 1 in which the compound of Formula (1) is of Formula (4):-



Formula (4)

- 45 in which:
- R³ is -H, -SO₂F, C₁₋₆-alkyl or C₁₋₆-alkoxy;
- R⁴ is -H, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy or -NHCOC₁₋₆-alkyl;
- 50 R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ each independently is -H, C₁₋₆-alkyl, C₁₋₆-alkoxy or -SO₂F; and
- R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ each independently is -H, -CN, -NO₂, -SO₂F, C₁₋₆-alkyl, C₁₋₆-alkoxy, -COC₁₋₆-alkyl, -COOC₁₋₆-alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² in which R¹ and R² are as hereinbefore defined except for 4-(2'-methoxyphenoxy)-4'-(4'-fluorosulphonylphenylazo)phenol.

- 55 8. A compound according to any one of Claims 5 to 7, characterized in that the compound carries at least one ester group or carries a substituent to which at least one ester group is attached.

9. A process for the mass coloration of plastics which comprises incorporating into a plastics material a compound or mixture thereof which is free from water solubilising groups, of Formula (1):

$$A-N=N-D-N=N-E \quad \text{Formula (1)}$$

in which

A, D and E each independently is an optionally substituted heterocyclic or carbocyclic group and at least one of A, D or E carries directly at least one $\text{-SO}_2\text{F}$ group or carries a substituent to which at least one $\text{-SO}_2\text{F}$ group is attached.

Patentansprüche

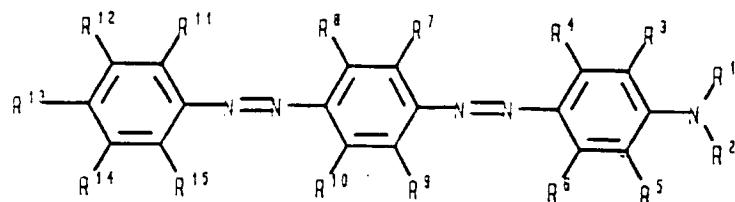
- 15 1. Verfahren zum Färben eines aromatischen Polyester-Textilmaterials oder eines Fasergemisches daraus, umfassend die Zugabe einer Verbindung zum aromatischen Polyester-Textilmaterial, die frei von wasserlöslichmachenden Gruppen der Formel (1) ist:

$$A-N = N-D-N = N-E \quad \text{Formel (1)}$$

worin:

A, D und E unabhängig voneinander jeweils eine gegebenenfalls substituierte, heterozyklische oder carbozyklische Gruppe sind und zumindest eines von A, D oder E zumindest eine direkt gebundene $-SO_2F$ -Gruppe trägt oder einen Substituenten trägt, an den zumindest eine $-SO_2F$ -Gruppe gebunden ist.

2. Verfahren nach Anspruch 1, worin die Verbindung der Formel (1) nachstehender Formel (2) entspricht:



Formel (2)

worin:

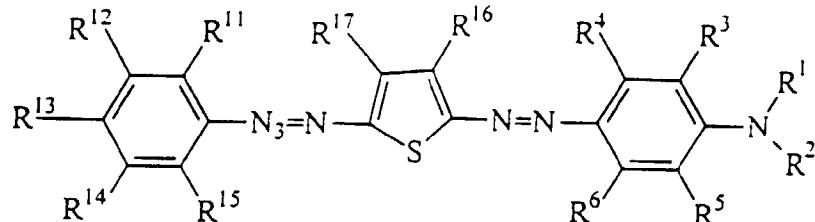
R¹ und R² jeweils unabhängig voneinander -H, C₁₋₆-Alkyl oder C₁₋₆-Alkyl substituiert mit -OH, -CN, -F, -Cl, -Br, -SO₂F, Phenyl, Phenyl-SO₂F, -OCO-C₁₋₆-Alkyl, -COO-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -COO-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, C₁₋₆-Alkoxy, C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -OC-C₁₋₆-Alkyl, -OC-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -OCO-(3-Fluorsulfonylphenyl), -OCO-(4-Fluorsulfonylphenyl), -OCO-Phenyl oder -OCO-C₂₋₄-Alkenyl sind;

R^3 -H, -SO₂F, C₁₋₆-Alkyl oder C₁₋₆-Alkoxy ist;

R^4 -H, - SO_2F , $C_{1-6}\text{-Alkyl}$, $C_{1-6}\text{-Alkoxy}$ oder $-\text{NH-CO-}C_{1-6}\text{-Alkyl}$ ist; R^3 , R^6 , R^7 , R^8 , R^9 und R^{10} jeweils unabhängig voneinander -H, $C_{1-6}\text{-Alkyl}$, $C_{1-6}\text{-Alkoxy}$ oder $-\text{SO}_2\text{F}$ sind; und R^{11} , R^{12} , R^{13} , R^{14} , R^{15}

R¹¹, R¹², R¹³, R¹⁴ und R¹⁵ jeweils unabhängig voneinander -H, -CN, -NO₂, -SO₂F, C₁₋₆-Alkyl, C₁₋₆-Alkoxy, -CO-C₁₋₆-Alkyl, -COO-C₁₋₆-Alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CO-NR¹R², -SO₂-NR¹R² sind, worin R¹ und R² wie oben definiert sind.

3. Verfahren nach Anspruch 1, worin die Verbindung der Formel (1) nachstehender Formel (3) entspricht:



(Formel 3)

worin:

15 R^1 und R^2 jeweils unabhängig voneinander -H, C₁₋₆-Alkyl oder C₁₋₆-Alkyl substituiert mit -OH, -F, -Cl, -Br, -SO₂F, Phenyl, Phenyl-SO₂F, -OCO-C₁₋₆-Alkyl, -COO-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -COO-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, C₁₋₆-Alkoxy, C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -OC-C₁₋₆-Alkyl, -OC-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -OCO-(3-Fluorsulfonylphenyl), -OCO-(4-Fluorsulfonylphenyl), -OCO-Phenyl oder -OCO-C₂₋₄-Alkenyl sind;

20 R^3 -H, -SO₂F, C₁₋₆-Alkyl oder C₁₋₆-Alkoxy ist;

R^4 -H, -SO₂F, C₁₋₆-Alkyl, C₁₋₆-Alkoxy oder -NH-CO-C₁₋₆-Alkyl ist;

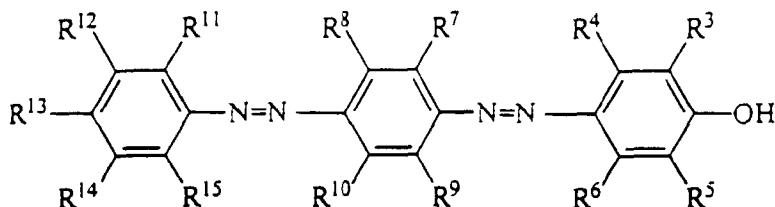
25 R^5 und R^6 jeweils unabhängig voneinander -H, C₁₋₆-Alkyl, C₁₋₆-Alkoxy oder -SO₂F sind;

R^{11} , R^{12} , R^{13} , R^{14} und R^{15} jeweils unabhängig voneinander -H, -CN, -NO₂, -SO₂F, C₁₋₆-Alkyl, C₁₋₆-Alkoxy, -CO-C₁₋₆-Alkyl, -COO-C₁₋₆-Alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CO-NR¹R², -SO₂-NR¹R² sind, worin R^1 und R^2 wie oben definiert sind;

30 R^{16} -H, -CN, -SO₂F, -COO-C₁₋₆-Alkyl, -CO-C₁₋₆-Alkyl oder -CO-NR¹R² ist, worin R^1 und R^2 wie oben definiert sind; und

R^{17} -H, -CN, -SO₂F oder C₁₋₆-Alkyl ist.

- 30 4. Verfahren nach Anspruch 1, worin die Verbindung der Formel (1) nachstehender Formel (4) entspricht:



(Formel 4)

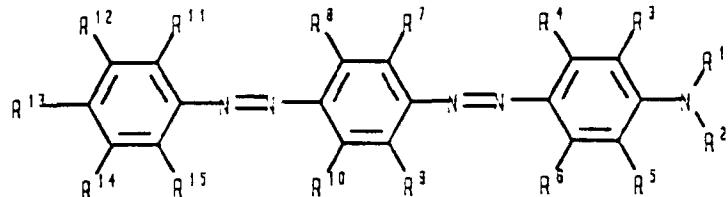
worin:

45 R^3 -H, -SO₂F, C₁₋₆-Alkyl oder C₁₋₆-Alkoxy ist;

R^4 -H, -SO₂F, C₁₋₆-Alkyl, C₁₋₆-Alkoxy oder -NH-CO-C₁₋₆-Alkyl ist;

50 R^5 , R^6 , R^7 , R^8 , R^9 und R^{10} jeweils unabhängig voneinander -H, C₁₋₆-Alkyl, C₁₋₆-Alkoxy oder -SO₂F sind; und R^{11} , R^{12} , R^{13} , R^{14} und R^{15} jeweils unabhängig voneinander -H, -CN, -NO₂, -SO₂F, C₁₋₆-Alkyl, C₁₋₆-Alkoxy, -CO-C₁₋₆-Alkyl, -COO-C₁₋₆-Alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CO-NR¹R², -SO₂-NR¹R² sind, worin R^1 und R^2 wie oben definiert sind.

- 55 5. Verbindung der Formel (1) wie in Anspruch 1 definiert, worin die Verbindung der Formel (1) nachstehender Formel (2) entspricht:



(Formel 2)

worin:

15 R¹ und R² jeweils unabhängig voneinander -H, C₁₋₆-Alkyl oder C₁₋₆-Alkyl substituiert mit -OH, -CN, -F, -Cl, -Br, -SO₂F, Phenyl, Phenyl-SO₂F, -OCO-C₁₋₆-Alkyl, -COO-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -COO-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, C₁₋₆-Alkoxy, C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -OC-C₁₋₆-Alkyl, -OC-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -OCO-(3-Fluorsulfonylphenyl), -OCO-(4-Fluorsulfonylphenyl), -OCO-Phenyl oder -OCO-C₂₋₄-Alkenyl sind;

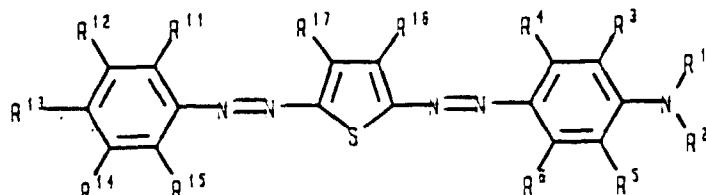
R³ -H, -SO₂F, C₁₋₆-Alkyl oder C₁₋₆-Alkoxy ist;

R⁴ -H, -SO₂F, C₁₋₆-Alkyl, C₁₋₆-Alkoxy oder -NH-CO-C₁₋₆-Alkyl ist;

20 R⁵, R⁶, R⁷, R⁸ und R¹⁰ jeweils unabhängig voneinander -H, C₁₋₆-Alkyl, C₁₋₆-Alkoxy oder -SO₂F sind; und

R¹¹, R¹², R¹³, R¹⁴ und R¹⁵ jeweils unabhängig voneinander -H, -CN, -NO₂, -SO₂F, C₁₋₆-Alkyl, C₁₋₆-Alkoxy, -CO-C₁₋₆-Alkyl, -COO-C₁₋₆-Alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CO-NR¹R², -SO₂-NR¹R² sind, worin R¹ und R² wie oben definiert sind.

- 25 6. Verbindung der Formel (1) wie in Anspruch 1 definiert, worin die Verbindung der Formel (1) nachstehender Formel (3) entspricht:



(Formel 3)

worin:

40 R¹ und R² jeweils unabhängig voneinander -H, C₁₋₆-Alkyl oder C₁₋₆-Alkyl substituiert mit -OH, -CN, -F, -Cl, -Br, -SO₂F, Phenyl, Phenyl-SO₂F, -OCO-C₁₋₆-Alkyl, -COO-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -COO-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, C₁₋₆-Alkoxy, C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -OC-C₁₋₆-Alkyl, -OC-C₁₋₆-Alkoxy-C₁₋₆-alkoxy, -OCO-(3-Fluorsulfonylphenyl), -OCO-(4-Fluorsulfonylphenyl), -OCO-Phenyl oder -OCO-C₂₋₄-Alkenyl sind;

R³ -H, -SO₂F, C₁₋₆-Alkyl oder C₁₋₆-Alkoxy ist;

R⁴ -H, -SO₂F, C₁₋₆-Alkyl, C₁₋₆-Alkoxy oder -NH-CO-C₁₋₆-Alkyl ist;

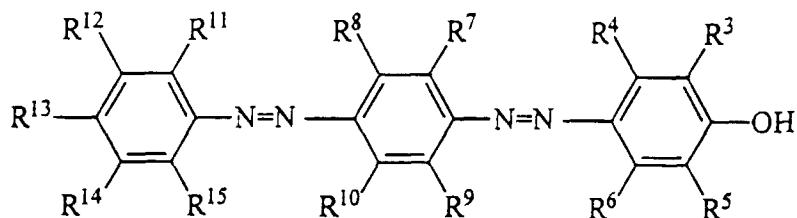
R⁵ und R⁶ jeweils unabhängig voneinander -H, C₁₋₆-Alkyl, C₁₋₆-Alkoxy oder -SO₂F sind;

45 R¹¹, R¹², R¹³, R¹⁴ und R¹⁵ jeweils unabhängig voneinander -H, -CN, -NO₂, -SO₂F, C₁₋₆-Alkyl, C₁₋₆-Alkoxy, -CO-C₁₋₆-Alkyl, -COO-C₁₋₆-Alkyl, -F, -Cl, -Br, -CF₃, -NR¹R², -CO-NR¹R², -SO₂-NR¹R² sind, worin R¹ und R² wie oben definiert sind;

50 R¹⁶ -H, -CN, -SO₂F, -COO-C₁₋₆-Alkyl, -CO-C₁₋₆-Alkyl oder -CO-NR¹R² ist, worin R¹ und R² wie oben definiert sind; und

R¹⁷ -H, -CN, -SO₂F oder C₁₋₆-Alkyl ist.

- 55 7. Verbindung von Formel (1) nach Anspruch 1, worin die Verbindung von Formel (1) nachstehender Formel (4) entspricht:



worin:

15 R^3 -H, $-SO_2F$, C_{1-6} -Alkyl oder C_{1-6} -Alkoxy ist;
 R^4 -H, $-SO_2F$, C_{1-6} -Alkyl, C_{1-6} -Alkoxy oder $-NH-CO-C_{1-6}$ -Alkyl ist;
 R^5 , R^6 , R^7 , R^8 , R^9 und R^{10} jeweils unabhängig voneinander -H, C_{1-6} -Alkyl, C_{1-6} -Alkoxy oder $-SO_2F$ sind; und
 R^{11} , R^{12} , R^{13} , R^{14} und R^{15} jeweils unabhängig voneinander -H, -CN, $-NO_2$, $-SO_2F$, C_{1-6} -Alkyl, C_{1-6} -Alkoxy,
 $-CO-C_{1-6}$ -Alkyl, $-COO-C_{1-6}$ -Alkyl, -F, -Cl, -Br, $-CF_3$, $-NR^1R^2$, $-CO-NR^1R^2$, $-SO_2-NR^1R^2$ sind, worin R^1 und R^2
20 wie oben definiert sind, mit Ausnahme von 4-(2'-Methoxyphenylazo-4'-(4'-fluorsulfonyl(phenylazo))phenol.

- 25
8. Verbindung nach einem der Ansprüche 5 bis 7, dadurch gekennzeichnet, daß die Verbindung zumindest eine Estergruppe trägt oder einen Substituenten trägt, an den eine Estergruppe gebunden ist.
 9. Verfahren zur deckenden Färbung von Kunststoffen, umfassend das Einarbeiten einer Verbindung oder eines Gemischs davon, die frei von wasserlöslichmachenden Gruppen ist und nachstehende Formel (1) aufweist:



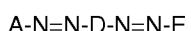
Formel (1)

30 worin:

35 A, D und E jeweils unabhängig voneinander eine gegebenenfalls substituierte, heterozyklische oder carbozyklische Gruppe sind und zumindest eines von A, D oder E zumindest eine direkt gebundene $-SO_2F$ -Gruppe trägt oder einen Substituenten trägt, an den zumindest eine $-SO_2F$ -Gruppe gebunden ist,
in ein Kunststoffmaterial.

Revendications

- 40
1. Procédé pour colorer une matière textile de polyester aromatique ou un mélange de fibres avec celui-ci, qui comprend l'application sur la matière textile de polyester aromatique d'un composé qui est exempt de groupes se solubilisant dans l'eau, de formule (1):

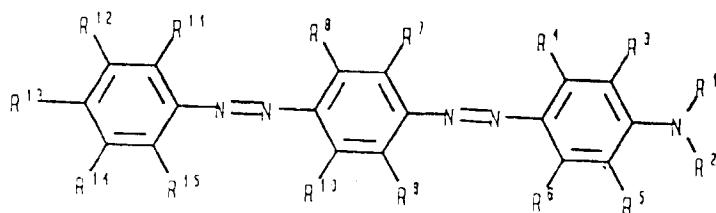


Formule (1)

dans laquelle :

50 A, D et E , chacun indépendamment, sont un groupe hétérocyclique ou carbocyclique facultativement substitué, et au moins l'un parmi A, D et E porte directement au moins un groupe $-SO_2F$ ou porte un substituant auquel au moins un groupe $-SO_2F$ est attaché.

- 55
2. Procédé selon la revendication 1, dans lequel le composé de formule (1) est de formule (2) :



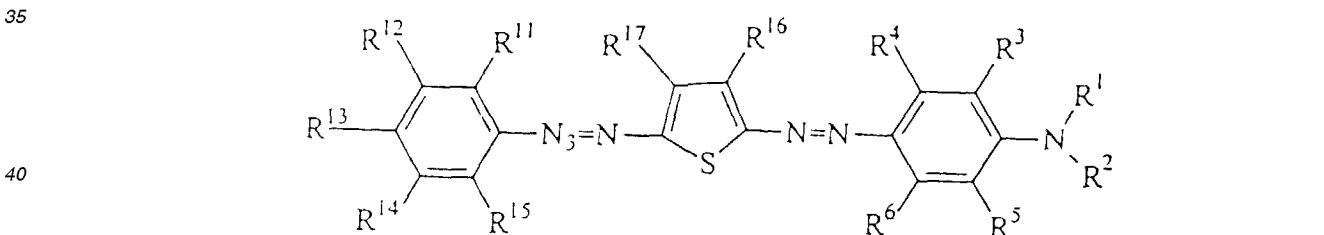
10

Formule (2)

dans laquelle :

- 15 R¹ et R², chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆ ou alkyle en C₁ à C₆ substitué par -OH, -CN, -F, -Cl, -Br, -SO₂F, un groupe phényle, phénylSO₂F, -OCO-alkyle en C₁ à C₆, -COO-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -COO-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, alcoxy en C₁ à C₆, alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -OC-alkyle en C₁ à C₆, -OC-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -OCO(3-fluorosulfonylphényle), -OCO(4-fluorosulfonylphényle), -OCOPhényle ou -OCO-alcényle en C₂ à C₄ ;
- 20 R³ est -H, -SO₂F, un groupe alkyle en C₁ à C₆ ou alcoxy en C₁ à C₆ ;
- R⁴ est -H, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -NHCO-alkyle en C₁ à C₆ ;
- 25 R⁵, R⁶, R⁷, R⁸, R⁹ et R¹⁰, chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -SO₂F ; et
- R¹¹, R¹², R¹³, R¹⁴ et R¹⁵, chacun indépendamment, sont -H, -CN, -NO₂, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆, -CO-alkyle en C₁ à C₆, -COO-alkyle en C₁ à C₆, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² où R¹ et R² sont tels que définis ci-dessus.
- 30

3. Procédé selon la revendication 1, dans lequel le composé de formule (1) est de formule (3) :



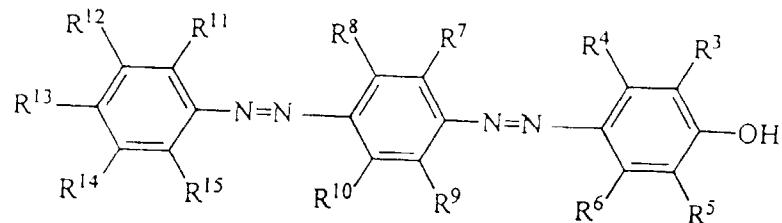
Formule (3)

- 45 dans laquelle :
- R¹ et R², chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆ ou alkyle en C₁ à C₆ substitué par -OH, -CN, -F, -Cl, -Br, -SO₂F, un groupe phényle, phénylSO₂F, -OCO-alkyle en C₁ à C₆, -COO-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -COO-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, alcoxy en C₁ à C₆, alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -OC-alkyle en C₁ à C₆, -OC-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -OCO(3-fluorosulfonylphényle), -OCO(4-fluorosulfonylphényle), -OCOPhényle ou -OCO-alcényle en C₂ à C₄ ;
- 50 R³ est -H, -SO₂F, un groupe alkyle en C₁ à C₆ ou alcoxy en C₁ à C₆ ;
- R⁴ est -H, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -NHCO-alkyle en C₁ à C₆ ;
- 55 R⁵ et R⁶, chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆, alcoxy en C₁

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R¹¹, R¹², R¹³, R¹⁴ et R¹⁵, à C₆ ou -SO₂F ;
 5 chacun indépendamment, sont -H, -CN, -NO₂, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆, -CO-alkyle en C₁ à C₆, -COO-alkyle en C₁ à C₆, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² où R¹ et R² sont tels que définis ci-dessus ;
 R¹⁶ est -H, -CN, -SO₂F, un groupe -COO-alkyle en C₁ à C₆, -CO-alkyle en C₁ à C₆ ou -CONR¹R² où R¹ et R² sont tels que définis ci-dessus ; et
 R¹⁷ est -H, -CN, -SO₂F ou un groupe alkyle en C₁ à C₆.

10 4. Procédé selon la revendication 1, dans lequel le composé de formule (1) est de formule (4) :

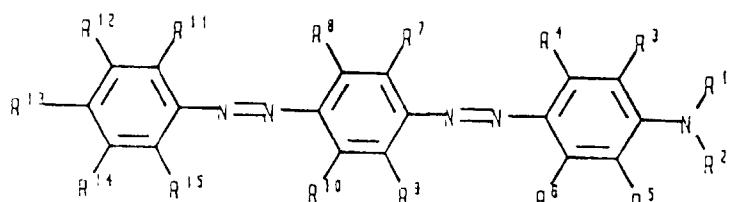


Formule (4)

dans laquelle :

25 R³ est -H, -SO₂F, un groupe alkyle en C₁ à C₆ ou alcoxy en C₁ à C₆ ;
 R⁴ est -H, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -NHCO-alkyle en C₁ à C₆ ;
 30 R⁵, R⁶, R⁷, R⁸, R⁹ et R¹⁰, chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -SO₂F ; et
 R¹¹, R¹², R¹³, R¹⁴ et R¹⁵, chacun indépendamment, sont -H, -CN, -NO₂, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆, -CO-alkyle en C₁ à C₆, -COO-alkyle en C₁ à C₆, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² où R¹ et R² sont tels que définis ci-dessus.

35 5. Composé de formule (1) selon la revendication 1, dans lequel le composé de formule (1) est de formule (2) :



Formule (2)

dans laquelle :

50 R¹ et R², chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆ ou alkyle en C₁ à C₆ substitué par -OH, -CN, -F, -Cl, -Br, -SO₂F, un groupe phényle, phénylISO₂F, -OCO-alkyle en C₁ à C₆, -COO-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -COO-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, alcoxy en C₁ à C₆, alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -OC-alkyle en C₁ à C₆, -OC-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -OC(3-fluorosulfonylphényle), -OC(4-fluorosulfonylphényle), -OCOPhényle ou -OCO-alcényle en C₂ à C₄ ;
 R³ est -H, -SO₂F, un groupe alkyle en C₁ à C₆ ou alcoxy en C₁ à C₆ ;

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R⁴

est -H, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -NHCO-alkyle en C₁ à C₆ ;

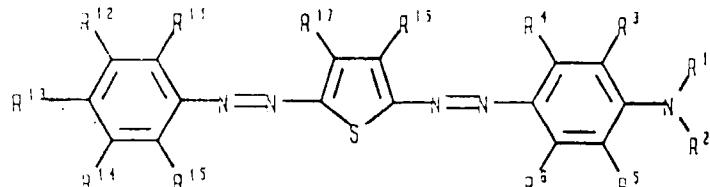
R⁵, R⁶, R⁷, R⁸, R⁹ et R¹⁰,

chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -SO₂F ; et

R¹¹, R¹², R¹³, R¹⁴ et R¹⁵,

chacun indépendamment, sont -H, -CN, -NO₂, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆, -CO-alkyle en C₁ à C₆, -COO-alkyle en C₁ à C₆, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² où R¹ et R² sont tels que définis ci-dessus.

10 **6.** Composé de formule (1) selon la revendication 1, dans lequel le composé de formule (1) est de formule (3) :



Formule (3)

dans laquelle :

R¹ et R²,

chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆ ou alkyle en C₁ à C₆ substitué par -OH, -CN, -F, -Cl, -Br, -SO₂F, un groupe phényle, phénylSO₂F, -OCO-alkyle en C₁ à C₆, -COO-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -COO-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, alcoxy en C₁ à C₆, alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -OC-alkyle en C₁ à C₆, -OC-alcoxy en C₁ à C₆-alcoxy en C₁ à C₆, -OC(3-fluorosulfonylphényle), -OC(4-fluorosulfonylphényle), -OCOPhényle ou -OCO-alcényle en C₂ à C₄ ;

R³

est -H, -SO₂F, un groupe alkyle en C₁ à C₆ ou alcoxy en C₁ à C₆ ;

R⁴

est -H, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -NHCO-alkyle en C₁ à C₆ ;

R⁵ et R⁶,

chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -SO₂F ;

R¹¹, R¹², R¹³, R¹⁴ et R¹⁵,

chacun indépendamment, sont -H, -CN, -NO₂, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆, -CO-alkyle en C₁ à C₆, -COO-alkyle en C₁ à C₆, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² où R¹ et R² sont tels que définis ci-dessus ;

R¹⁶

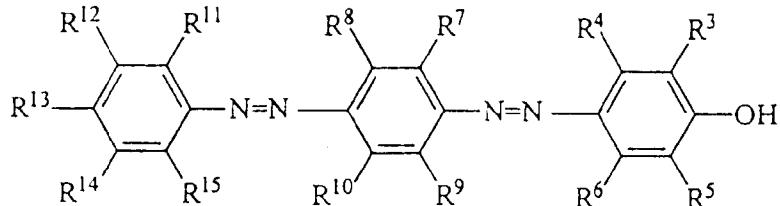
est -H, -CN, -SO₂F, un groupe -COO-alkyle en C₁ à C₆, -CO-alkyle en C₁ à C₆ ou -CONR¹R² où R¹ et R² sont tels que définis ci-dessus ; et

R¹⁷

est -H, -CN, -SO₂F ou un groupe alkyle en C₁ à C₆.

7. Composé de formule (1) selon la revendication 1, dans lequel le composé de formule (1) est de formule (4) :

45



Formule (4)

dans laquelle :

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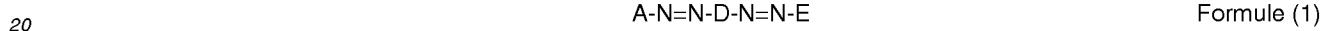
R³ est -H, -SO₂F, un groupe alkyle en C₁ à C₆ ou alcoxy en C₁ à C₆ ;
R⁴ est -H, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -NHCO-alkyle en C₁ à C₆ ;

5 R⁵, R⁶, R⁷, R⁸, R⁹ et R¹⁰, chacun indépendamment, sont -H, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆ ou -SO₂F ; et

10 R¹¹, R¹², R¹³, R¹⁴ et R¹⁵, chacun indépendamment, sont -H, -CN, -NO₂, -SO₂F, un groupe alkyle en C₁ à C₆, alcoxy en C₁ à C₆, -CO-alkyle en C₁ à C₆, -COO-alkyle en C₁ à C₆, -F, -Cl, -Br, -CF₃, -NR¹R², -CONR¹R², -SO₂NR¹R² où R¹ et R² sont tels que définis ci-dessus, sauf le 4-(2'-méthoxyphénylazo)-4'-(4'-fluorosulfony(phénylazo)) phénol.

8. Composé selon l'une quelconque des revendications 5 à 7, caractérisé en ce que le composé porte au moins un groupe ester ou porte un substituant auquel au moins un groupe ester est attaché.

15 9. Procédé pour la coloration de matières plastiques dans la masse, qui comprend l'incorporation dans une matière plastique d'un composé ou d'un mélange de celui-ci qui est exempt de groupes se solubilisant dans l'eau, de formule (1):



dans laquelle :

25 A, D et E , chacun indépendamment, sont un groupe hétérocyclique ou carbocyclique facultativement substitué, et au moins l'un parmi A, D et E porte directement au moins un groupe -SO₂F ou porte un substituant auquel au moins un groupe -SO₂F est attaché.

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